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Abstract

Sharp leading edges and nose caps on hypersonic vehicles, re-entry vehicles and reusable launch vehicles are items of current research interest for enhanced aerodynamic performance and maneuverability. The unique combination of mechanical properties, physical properties, thermal / electrical conductivities and thermal shock resistance of ZrB_2 make it a promising candidate material for such applications. In the recent past, a lot of work has been carried out on ZrB_2-based materials towards processing as well as characterization of their mechanical, oxidation and thermal behaviour. ZrB_2 based materials have been successfully processed by conventional hot pressing, pressureless sintering, reactive hot pressing and spark plasma sintering. Densification of ZrB_2 gets activated when the oxide impurities (B_2O_3 and ZrO_2) were removed from particle surfaces, which minimized coarsening. B_4C is widely used as a sintering additive for ZrB_2 because it reduces ZrO_2 at low temperature. It is found that full densification in ZrB_2 based materials by hot pressing is achieved either at 2000 ^{0}C and higher temperatures with moderate pressure of 20-30 MPa or at reduced temperature (1790-1840 ^{0}C) with much higher pressure (800-1500 MPa). But no study is available that identifies the dominant hot pressing mechanism at different temperatures and pressures. On the other hand, reinforcement of SiC in ZrB_2 is known to increase flexural strength, fracture toughness and oxidation resistance. It has been shown that oxidation resistance of ZrB_2-SiC composites is superior to that of monolithic ZrB_2 and SiC. For high temperature applications in air, the residual strength (room temperature strength after exposure in air at high temperatures) of non oxide ceramics after oxidation is important. A few reports are available on residual strength of ZrB_2 –SiC composite after thermal exposure at high temperatures. In contrast to the literature on composites**,** there are no reports

available on the residual strength of monolithic ZrB_2 after exposure to high temperatures. Also, previous studies on residual strength of ZrB_2-SiC composites have been limited to a single temperature of exposure. But there is a need to measure the residual strength after exposure to a range of temperatures since the oxide layer structure changes with temperature. The room temperature thermal conductivity data for ZrB_2 and ZrB_2-SiC composite shows a wide scatter in value as well as a dependence on microstructural parameters, especially porosity and grain size. Also, there is insufficient data available for the high temperature thermal conductivity of ZrB_2-SiC. Therefore, it is difficult to evaluate the effect of SiC content on thermal conductivity of ZrB_2-SiC composites at high temperatures. The present thesis seeks to address some of these gaps to better understand the suitability of ZrB_2 and ZrB_2-SiC composites for ultra-high temperature applications.

In the present work, hot pressing is used for densification of ZrB_2 and ZrB_2-SiC composites. Different amounts of B_4C (0, 0.5, 1, 3 & 5 wt %) were used as sintering additives in ZrB_2 and hot pressed at 2000 ^{0}C with 25 MPa applied pressure. The hot pressed samples are characterized for their microstructural, mechanical properties and oxidation behaviour. By addition of B_4C, density as well as micro-hardness increased. For lower B_4C content (0.5 & 1 wt %), hot pressed ZrB_2 has shown considerable improvement in flexural strength after exposure in air at 1000 ^{0}C for 5 hours, while higher B_4C content (3 & 5 wt %) leads to marginal or no improvement.

Due to the better mechanical and oxidation behavior of composites containing SiC, the densification behavior during hot pressing was studied. The densification behaviors as well as the microstructures for hot pressing of ZrB_2-20 % SiC composite were found to change in a very narrow temperature range. During hot pressing at 1700 ^{0}C, the densification was found to be mechanically driven particle fragmentation and rearrangement. On the other hand, thermally

activated mass transport mechanisms started dominating after initial particle fragmentation and rearrangement after hot pressing at 1850 ^{0}C and 2000 ^{0}C. At 2000 ^{0}C, the rate of grain boundary diffusion was enhanced which resulted into annihilation of dislocation.

The effect of SiC contents (10, 20 & 30 vol %) on mechanical and oxidation behavior of ZrB_2-SiC composite were also studied. The average micro-hardness and fracture toughness of ZrB_2-SiC composites increased with SiC content. But the flexural strength of ZrB_2- 20 vol % SiC composites was found to be the highest. Oxidation and residual strength of hot pressed ZrB_2 -SiC composites were evaluated as a function of SiC contents after exposure over a wide temperature range (1000-1700 ^{0}C). Multilayer oxide scale structures were found after oxidation. The composition and thickness of these multilayered oxide scale structures were found to depend on exposure temperature and SiC content. After exposure to 1000 ^{0}C for 5 hours, the residual strength of ZrB_2 -SiC composites improved by nearly 60 % compared to the as-hot pressed composites with 20 & 30 vol % SiC. On the other hand, the residual strength of these composites remained unchanged after 1500 ^{0}C for 5 hours. A drastic degradation in residual strength was observed in composites with 20 & 30 vol % SiC whereas strength was retained for ZrB_2-10 % SiC composite after exposure to 1700 ^{0}C for 5 hours in ZrB_2 –SiC. Therefore, residual strength of ZrB_2-10 % SiC composite was measured at different exposure times (up to 10 hours) at 1500 ^{0}C. An attempt was made to correlate the microstructural changes and oxide scales with residual strength with respect to variation in SiC content and temperature of exposure. Since the ZrB_2- 20 vol % SiC composite showed the maximum strength, the dependence of strength on various microstructural as well processing parameters was also studied. It was found that porosity, grain size as well as surface residual stress due to grinding influenced the strength of ZrB_2- 20 vol % SiC composites.

Finally, thermal diffusivity and conductivity of hot pressed ZrB_2 with different amounts of B_4C and ZrB_2-SiC composites were investigated experimentally over a wide temperature range (25 – 1500 ^{0}C). Both thermal diffusivity as well as thermal conductivity was found to decrease with increase in temperature for all hot pressed ZrB_2 and ZrB_2-SiC composites. At around 200 ^{0}C, thermal conductivity of ZrB_2-SiC composites was found to be composition independent. Thermal conductivity of ZrB_2-SiC composites was also correlated with theoretical predictions of the Maxwell- Eucken relation. The dominated mechanisms of heat transport for all hot pressed ZrB_2 and ZrB_2-SiC composites at room temperature were determined by Wiedemann-Franz analysis using measured room temperature electrical conductivity of these materials. It was found that the electronic thermal conductivity dominated for all monolithic ZrB_2 whereas the phonon contribution to thermal conductivity increased with SiC contents for ZrB_2-SiC composites. The heat conduction mechanism at high temperature was also studied by measuring the high temperature electrical conductivity of ZrB_2 and ZrB_2-SiC composites. The effect of porosity on thermal diffusivity and conductivity was also studied for ZrB_2- 20 vol % SiC composites.